Brief Communications

ESR study of the effect of fluorinated alcohols on magnetic resonance parameters of spin-adducts of phosphoryl radicals with products of cycloaddition of substituted nitriloxides to C_{60}

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Regioselectivity of the addition of phosphoryl radicals to the products of cycloaddition of substituted nitriloxides to fullerene C_{60} was studied by ESR spectroscopy. The effect of fluorine-containing alcohols on the magnetic resonance parameters of the isomers of spin-adducts of phosphoryl radicals located at different distances from the five-membered heterocycle was studied. Complexation of the obtained isomeric spin-adducts with $(CF_3)_3COH$ leads to a 3 to 5 G increase in the constant of hyperfine interaction with the phosphorus nucleus, which makes it possible to observe additional lines in the ESR spectrum.

Key words: ESR spectra, radical, phosphoryl, fullerene, heterocycles, isomers, complexation, fluorinated alcohol.

The influence of fluorine-containing alcohols on magnetic resonance parameters of phosphorylfullerenyl radicals that we found recently[1] can be useful in the analysis of the ESR spectra of spin-adducts of phosphoryl radicals with fullerene derivatives, especially in those cases where superposition of the ESR lines of several isomers is observed. The interest in studying regioselectivity of addition of phosphoryl radicals to fullerene derivatives is associated with the fact that it is possible to judge the character of the organic ligand—fullerene bond and to establish the regularities of the distribution of regioisomers depending on the nature of the organic ligand on the basis of the spectral pattern.[2–4] The rate of the addition of phosphoryl radicals to fullerene derivatives can appear to be higher than that of the addition to fullerene. For this reason, in the case of fullerene derivatives there is a

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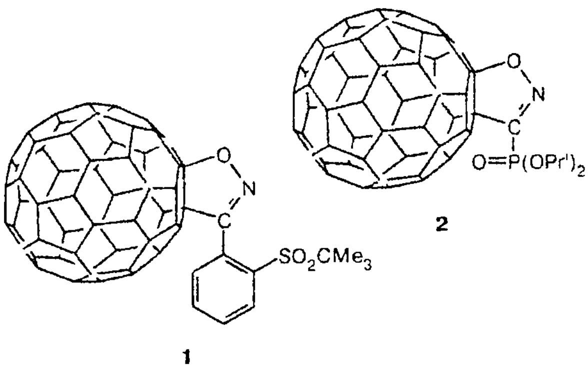
theoretical possibility of the formation of polyaddition adducts of phosphoryl radicals, which are characterized by isomers with different numbers and positions of phosphoryl groups, even under conditions of the formation of monoadducts of phosphoryl radicals with C_{60}. Hence, the interpretation of ESR spectra of the spin-adducts of phosphoryl radicals with fullerene derivatives can appear to be ambiguous. Addition of a fluorinated alcohol, which shifts the equilibrium towards monoadducts of phosphoryl radicals,[1] must eliminate this problem. In addition, increase in the constants of HFI with the nucleus of a phosphorus atom in the spin-adducts of phosphoryl radicals with fullerene derivatives in the presence of fluorinated alcohols will make it possible to observe additional lines that were overlapped with other lines in the absence of alcohol.

Experimental

The solutions studied were irradiated with the focussed light of a DRSh-1000 high-pressure mercury lamp. ESR spectra were recorded on a Varian E-12A spectrometer. The specimens were thermostatted using a Unipan electronic temperature controller.

Results and Discussion

We studied the ESR spectra of spin-adducts of phosphoryl radicals with the following C_{60} derivatives:



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The addition of the phosphoryl radicals obtained by photolysis of $Hg[P(O)(OPr^i)_2]_2$ in saturated toluene solution of compound **1** (its synthesis was reported earlier[5]) results in the formation of a mixture of isomers (**1a**—**e**), in which the phosphoryl group is at different distances from the organic substituent. The ESR spectrum (Fig. 1, *a*) shows that the isomers differ not only in their HFI constants, but also in the *g*-factors, *viz.*, **1a**, a_P = 52.75 G, g = 2.0021; **1b**, a_P = 62.25 G, g = 2.0021; **1c**, a_P = 66.5 G, g = 2.0025; **1d**, a_P = 72.5 G; and **1e**, a_P = 75.0 G (determination of the *g*-factors for the last two isomers is difficult because of superposition of their ESR spectra). This leads to an asymmetric pattern of superposition of high-field and low-field components of the phosphorus doublets for isomers **1a**—**c**. It can be assumed that the shift of the *g*-factor of isomer **1c** compared to those of isomers **1a** and **1b** is caused by the interaction of the unpaired electron with the nucleus of the oxygen atom, which means that the phosphoryl group in isomer **1c** is at a distance of two or three bonds from the O atom. No conformational isomerism is observed as temperature decreases. Possibly, this is due to the line broadening caused by slower rotation of the phosphorylfullerenyl radicals containing an organic group.

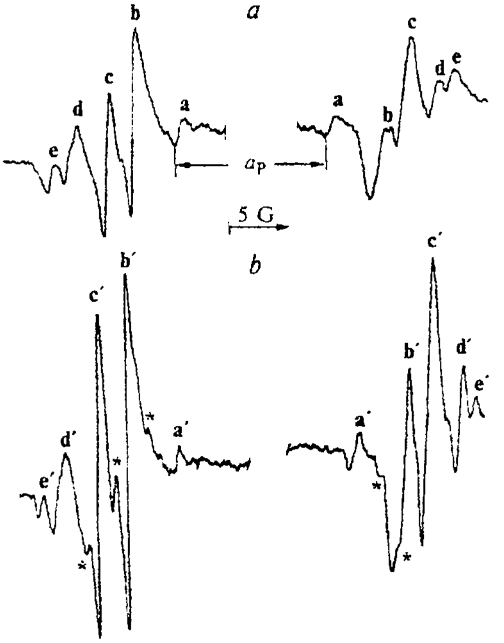

Fig. 1. ESR spectra of isomers **1a**—**e** (*a*) and **1a'**—**e'** (*b*) (here and in Fig. 2 the lines not observed before addition of $(CF_3)_3COH$ are asterisked).

In the case of photochemical generation of the spin-adducts of phosphoryl radicals with compound **1** in an alcohol—toluene solution containing 5% $(CF_3)_3COH$, the constants of HFI with the nuclei of phosphorus atoms in isomers (**1a'**—**e'**) increase proportionally to the constants of HFI with the nuclei of phosphorus atoms not bound in the complex by radicals (Fig. 1, *b*): **1a'**, a_P = 56.25 G, g = 2.002; **1b'**, a_P = 66.12 G, g = 2.002; **1c'**, a_P = 71.12 G, g = 2.0023; **1d'**, a_P = 78.5 G; and **1e'**, a_P = 80.75 G. This makes it possible to observe additional lines (they are asterisked in Fig. 1, *b*).

Then we studied the spin-adducts of C_{60} derivative **2** containing a phosphoryl group in the cycle (see Ref. 6). Photolysis of diphosphorylmercury compound in saturated toluene solution of **2** results in the formation of a mixture of isomers (**2a**—**f**) characterized by the following magnetic resonance parameters (Fig. 2, *a*): **2a**, a_P = 52.9 G, g = 2.0022; **2b**, a_P = 58.25 G, g = 2.0022; **2c**, a_P = 62.25 G, g = 2.0021; **2d**, a_P = 64.5 G, g = 2.0022; **2e**, a_P = 67.25 G, g = 2.0021; and **2f**, a_P = 73.5 G, g = 2.002.

From the above data it can be seen that, in contrast to the isomers of the spin-adducts of **1**, the low-field and

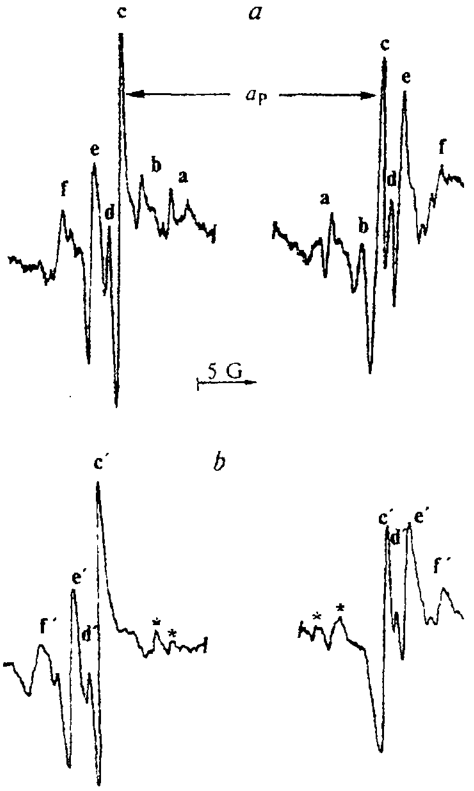

Fig. 2. ESR spectra of isomers **2a—f** (*a*) and **2c′—f′** (*b*).

high-field multiplets in the ESR spectra of spin-adducts of **2** are symmetric and, hence, these adducts contain no isomer in which the phosphoryl group is neighboring the oxygen atom.

Addition of $(CF_3)_3COH$ in the ratio indicated above results in increase in the constants of HFI with the nucleus of the phosphorus atom in isomers **2c′—2f′** (Fig. 2, *b*): **2c′**, a_P = 65.75 G, g = 2.0021; **2d′**, a_P = 68.0 G, g = 2.0022; **2e′**, a_P = 70.75 G, g = 2.0021; and **2f′**, a_P = 77.5 G, g = 2.002. Disappearance of isomers **2a** and **2b** is likely due to the fact that they are adducts of polyaddition of phosphoryl radicals (*cf.* Ref. 1).

As was shown previously,[2] studying the radical $\rightleftharpoons$ dimer equilibrium for individual isomers is one of the most reliable methods for determination of the position of addition of phosphoryl radicals with respect to the organic substituent. The shorter the distance between the position to which the phosphoryl radical is added and the substituent, the higher the shielding of the fullerenyl radical that forms and the lower the enthalpy of the radical $\rightleftharpoons$ dimer equilibrium. In the case of isomers of radical **2**, switching off the irradiation leads to disappearance of all radicals (over ~1 s), except for isomer **2c′**, whose fraction decreases to a constant level corresponding to ~10% of the initial amount. The lifetime of this isomer is ~ 1 min. Based on the above data, it can be assumed that it is in radical **2c′** that the phosphoryl group added is at the shortest distance from the heterocycle (possibly, at a distance of two or three bonds from the heterocycle). It should be noted that the intensity of the signal of **2c′** is ~50% of the total intensity of the signals of other isomers.

Thus, the composition and fractions of isomeric spin-adducts are changed depending on the nature of the substituent in the heterocycle. The effect of fluorinated alcohols on the magnetic resonance parameters of fullerenyl radicals can be used in the analysis of the regioselectivity of addition of phosphoryl radicals to organic fullerene derivatives.

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